CLAIMS

1. Supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups up to four reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds.

2. Supramolecular polymer (c) and (c') according to claim 1 comprising quadruple hydrogen bonding units in the polymer backbone, said supramolecular polymer (c) and (c') having a structure according to formula (I) or formula (II):

$\{(a)_p\text{–}(b)_q\}_v$ [I]

$\{(a)_p\text{–}(b')_q\}_w$ [II]

wherein:

(a) is a monomeric unit that comprises a (precursor of) 4H-element;

(b) is a macromonomeric unit;

(b') is a fragmented part of the original polymer (b);

(a) and (b) are connected, preferably covalently, in the polymer backbone;

p and q indicate the total number of units of (a) and (b) or (a) and (b') in the polymer backbone;

p is 1 to 100;

q is 0 to 20;

v is the number of repeating units of the connected monomeric units (a) and the connected macromonomeric units (b);

w is the number of repeating units of the connected monomeric units (a) and the connected macromonomeric units (b');

macromonomeric unit (b) has a number average molecular weight of at least about 100 to about 100000;

macromonomeric unit (b') has a number average molecular weight of at least about 50 to about 20000;

polymer (c) has a number average molecular weight of about 2000 to about 80000;.

polymer (c') has a number average molecular weight of about 2000 to about 80000;

provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds.

3. Supramolecular polymer according to claim 1 or claim 2, wherein the monomeric unit (a) comprises a (precursor of a) 4H-unit and comprises at least two reactive groups up to four reactive groups.

4. Supramolecular polymer acxcording to any one of claims 1 - 3, wherein the macromonomeric unit (b) comprises at least two complementary reactive groups up to six complementary reactive groups.

5. Supramolecular polymer according to any one of claims 1 - 4, wherein the amount of 4H-units incorporated in the polymer backbone is about 33 to about 66 mol %, based on the total amount of moles of (a) and (b) or (a) and (b').

6. Supramolecular polymer according to any one of claims 1 - 5, wherein the monomeric unit (a) has a structure according to formula (III) or (IV):

$$4H - (F_i)_r \qquad (III)$$

$$4H^* - (F_i)_r \qquad (IV)$$

wherein F_i comprises a reactive linked to the 4H-unit or 4H*-unit; and r is in the range of 1 to 4.

7. Supramolecular polymer according to claim 6, wherein r is 2.

8. Supramolecular polymer according to any one of claims 1 - 7, wherein the macromonomeric unit (b) is represented by formula (V):

$$P–(F_i)_s \qquad (V)$$

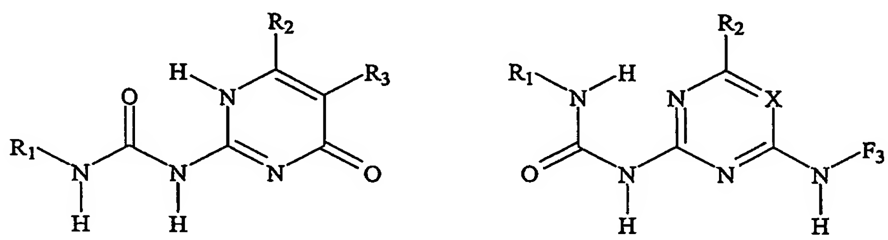
wherein:

P represents a polymer chain having a number average molecular weight of 100 to 100000;

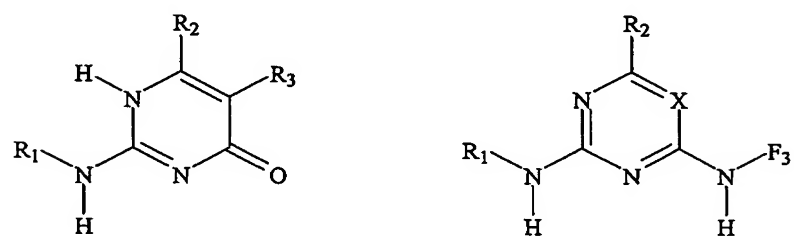
F_i represents a complementary reactive group in the macromonomeric unit (b) that is complementary reactive with another F_i of monomeric unit (a): and

s represents the number of these groups in the macromonomer and is 0 - 6 preferably 2 - 6.

9. Supramolecular polymer according to any one of claims 1 - 8, wherein the monomeric unit (a) has a structure according to formula (VI) or formula (VII) and tautomers and/or enantiomers thereof:



(VI)

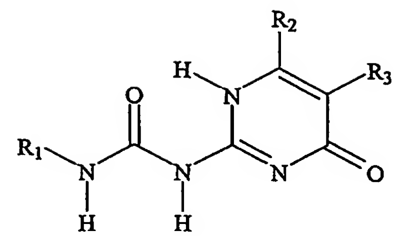


(VII)

wherein R1 - R4 are selected from the group consisting of hydrogen atoms and shorter or longer chains, the longer and shorter chains being selected from the group consisting of saturated or unsaturated, branched, cyclic or linear alkyl chains, aryl chains, alkaryl chains, arylalkyl chains, ester chains or ether chains and wherein X is a nitrogen atom or a carbon atom to which a group R4 is attached.

10. Supramolecular polymer according to claim 9, wherein R1 - R4 are selected from the group consisting of random side chains and hydrogen atoms, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms.

11. Supramolecular polymer according to claim 9, wherein the monomeric unit (a) is represented by formula (VIa):



(VIa)

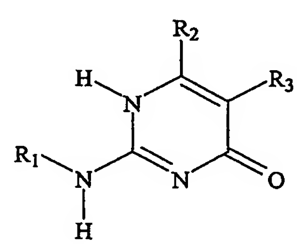
wherein:

(a) the 4H-unit is connected to a reactive group (F_1) via R1 and a reactive group (F_1) or (F_2) via R2, whereas R3 is a random side chain or a hydrogen atom, the random side chain being being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

(b) the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

(c) the 4H-unit is connected to two reactive groups (F_i) both via R1, whereas R2 and R3 are random side chain or hydrogen atoms, the random side chains being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms.

12. Supramolecular polymer according to claim 9, wherein in the structure according to formula (VIIa):



(VIIa)

wherein:

(a) the 4H-unit is connected to a reactive group (F_1) via R1 and a reactive group (F_1) or (F_2) via R2, whereas R3 is a random side chain or a

hydrogen atom, the random side chain being being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

(b) the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms.

13. Supramolecular polymer according to any one of the preceding claims, wherein the macromonomeric unit (b) has a structure according to formula (VIII):

$$F2 - P - F2 \text{ or } F1 - P - F2 \qquad (VIII)$$

wherein:

P is selected from the group consisting of polyesters, polyether, polycarbonates and hydrogenated polyolefins; and

F_1 and F_2 are independently selected from the group consisting of -OH, -NH_2, -NCO and -C=CH_2.

14. Supramolecular polymer according to claim 13, wherein P has a number average molecular weight of 100 to 100000.

15. Supramolecular polymer according to claim 13, wherein P has a number average molecular weight of 5000 to 100000.

16. A process for the preparation of a supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups up to four reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds, wherein a monomeric unit (a) having a structure according to formulae (III) or (IV) and a macromonomeric unit (b) having a structure according to formulae (V) are reacted.

17. Process according to claim 16, wherein the process proceeds by chain extension and wherein the following sets of monomeric unit (a) and macromonomeric unit (b) are polymerised:

(a) F_1-4H-F_1 and F_3-P-F_3;

(b) F_1-4H-F_2 and F_3-P-F_3;

(c) F_1-4H*-F_1 and F_3-P-F_3; or

(d) F_1-4H*-F_2 and F_3-P-F_3

wherein the couples F_1 - F_3 and F_2 - F_3 are complementary reactive groups.

18. Process according to claim 17, wherein the reactive groups F_i are selected from the group consisting of -NH_2, -NHR, -NCO, blocked -NCO, -OH, -C(O)OH, -C(O)OR wherein R is a linear or branched C_1-C_6 alkyl group, a C_6 - C_{12} arylgroup, a C_7 - C_{12} alkaryl group or a C_7 - C_{12} alkylaryl group, or R is halogen atom selected from the group consisting of Cl, Br or I.

19. Process according to any one of claims 16 - 18, wherein two or more macromonomeric units (b) having a different number average molecular weight are used.

20. Process according to any one of claims 16 - 18, wherein two or more macromonomeric units (b) having a different molecular structure are used.

21. Process according to any one of claims 16 - 18, wherein the monomeric unit (a) and/or the macromonomeric unit (b) comprises a "stopper" moiety having the formula P-F_1, 4H-F_1 of 4H*-F_1, wherein F_1, 4H and 4H* are as defined in the preceding claims.

22. Process according to any one of claims 16 - 18, wherein branching species of monomeric unit (a) or macromonomeric unit (b) are used, said branching species having the formula P-$(F_i)_u$ or 4H-$(F_i)_u$ or 4H*-$(F_i)_u$, wherein u is 3 - 6.

23. Process according to any one of claims 16 - 22, wherein the molar ratio between monomeric unit (a) and macromonomeric unit (b) is between 1:2 and 2:1.

24. Process according to claim 16, wherein the process proceeds by redistribution and wherein the following sets of monomeric unit (a) and macromonomeric unit (b) are polymerised:

(a) F_1-4H-F_1 and P; or

(b) F_1-4H-F_2 and P

wherein F_1, F_2 and P are as defined in the preceding claims.

25. Process according to claim 24, wherein P has an number average molecular weight of 5000 - 100000.

26. Process according to claim 24 or claim 25, wherein the molar ratio between monomeric unit (a) and macromonomeric unit (b) is between 3:1 and 10:1.

27. A supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds, said supramolecular polymer being obtainable by the process according to any one of claims 16 - 26.

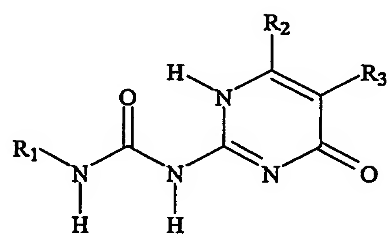
28. Use of a supramolecular polymer according to claims 1 - 15 or 27 in personal care applications, surface coatings, imaging technologies, biomedical applications, (thermo)reversible coatings, adhesive and sealing compositions and as thickening agents, gelling agents and binders.

AMENDED CLAIMS
[Received by the International Bureau on 14 May 2004 (14.05.04):
original claims 1-28 replaced by new claims 1-25 (8 pages)]

1. Supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups up to four reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds,
wherein the monomeric unit (a) has a structure according to formula (III) or (IV):

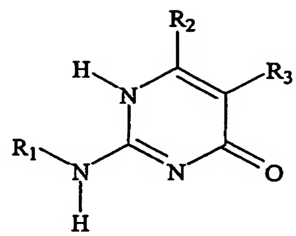
$$4H - (F_i)_r \quad \text{(III)}$$
$$4H^* - (F_i)_r \quad \text{(IV)}$$

wherein F_i comprises a reactive group linked to the 4H-unit or 4H*-unit; and r is 2;
wherein the monomeric unit (a) is represented by formula (VIa):



(VIa)

wherein:
(a) the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or
(b) the 4H-unit is connected to two reactive groups (F_i) both via R1, whereas R2 and R3 are random side chain or hydrogen atoms, the random side chains being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or
wherein the monomeric unit (a) is represented by formula (VIIa):



(VIIa)

wherein the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; and

wherein R1 – R3 are selected from the group consisting of hydrogen atoms and shorter or longer chains, the longer and shorter chains being selected from the group consisting of saturated or unsaturated, branched, cyclic or linear alkyl chains, aryl chains, alkaryl chains, arylalkyl chains, ester chains or ether chains.

2. Supramolecular polymer (c) and (c') according to claim 1 comprising quadruple hydrogen bonding units in the polymer backbone, said supramolecular polymer (c) and (c') having a structure according to formula (I) or formula (II):

$\{(a)_p-(b)_q\}_v$ [I]

$\{(a)_p-(b')_q\}_w$ [II]

wherein:

(a) is a monomeric unit that comprises a (precursor of) 4H-element;

(b) is a macromonomeric unit;

(b') is a fragmented part of the original polymer (b);

(a) and (b) are connected, preferably covalently, in the polymer backbone;

p and q indicate the total number of units of (a) and (b) or (a) and (b') in the polymer backbone;

p is 1 to 100;

q is 0 to 20;

v is the number of repeating units of the connected monomeric units (a) and the connected macromonomeric units (b);

w is the number of repeating units of the connected monomeric units (a) and the connected macromonomeric units (b');

macromonomeric unit (b) has a number average molecular weight of at least about 100 to about 100000;

macromonomeric unit (b') has a number average molecular weight of at least about 50 to about 20000;

polymer (c) has a number average molecular weight of about 2000 to about 80000;.

polymer (c') has a number average molecular weight of about 2000 to about 80000;

provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds.

3. Supramolecular polymer according to claim 1 or claim 2, wherein the macromonomeric unit (b) comprises at least two complementary reactive groups up to six complementary reactive groups.

4. Supramolecular polymer according to any one of claims 1 - 3, wherein the amount of 4H-units incorporated in the polymer backbone is about 33 to about 66 mol %, based on the total amount of moles of (a) and (b) or (a) and (b').

5. Supramolecular polymer according to any one of claims 1 - 4, wherein the macromonomeric unit (b) is represented by formula (V):

$$P\text{–}(F_i)_s \qquad (V)$$

wherein:

P represents a polymer chain having a number average molecular weight of 100 to 100000;

F_i represents a complementary reactive group in the macromonomeric unit (b) that is complementary reactive with another F_i of monomeric unit (a): and

s represents the number of these groups in the macromonomer and is 0 - 6 preferably 2 - 6.

6. Supramolecular polymer according to any one of the preceding claims, wherein the macromonomeric unit (b) has a structure according to formula (VIII):

$$F2 - P - F2 \text{ or } F1 - P - F2 \qquad \text{(VIII)}$$

wherein:

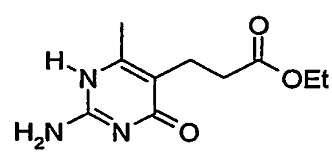
P is selected from the group consisting of polyesters, polyether, polycarbonates and hydrogenated polyolefins; and

F_1 and F_2 are independently selected from the group consisting of -OH, -NH_2, -NCO and -C=CH_2.

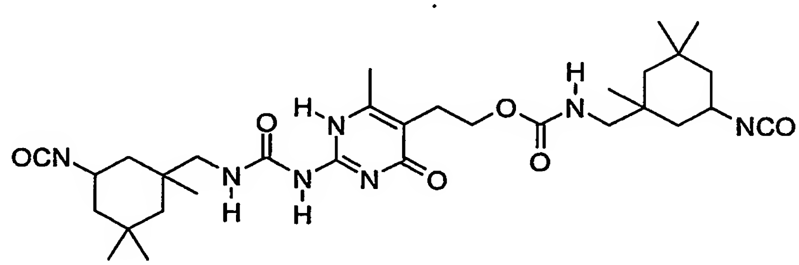
7. Supramolecular polymer according to claim 6, wherein P has a number average molecular weight of 100 to 100000.

8. Supramolecular polymer according to claim 6, wherein P has a number average molecular weight of 5000 to 100000.

9. Supramolecular polymer according to any one of claims 1 – 8, wherein the monomeric unit (a) is



10. Supramolecular polymer according to any one of claims 1 – 8, wherein the monomeric unit (a) is



11. A process for the preparation of a supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups up to four reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds, wherein a monomeric unit (a) having a structure according

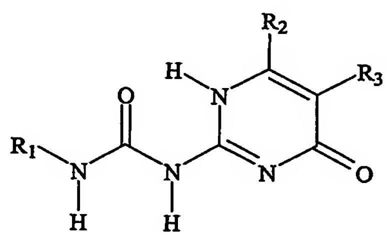
to formulae (III) or (IV) and a macromonomeric unit (b) having a structure according to formulae (V) are reacted,

wherein the monomeric unit (a) has a structure according to formula (III) or (IV):

$$4H - (F_i)_r \quad (III)$$
$$4H^* - (F_i)_r \quad (IV)$$

wherein F_i comprises a reactive group linked to the 4H-unit or 4H*-unit; and r is 2;

wherein the monomeric unit (a) is represented by formula (VIa):



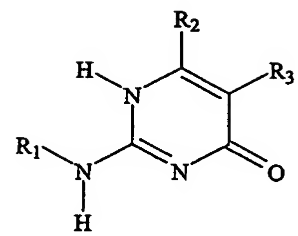
(VIa)

wherein:

(c) the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

(d) the 4H-unit is connected to two reactive groups (F_i) both via R1, whereas R2 and R3 are random side chain or hydrogen atoms, the random side chains being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; or

wherein the monomeric unit (a) is represented by formula (VIIa):



(VIIa)

wherein the 4H-unit is connected to a reactive group (F_1) via R1 and to a reactive group (F_1) or (F_2) via R3, whereas R2 is a random side chain or a hydrogen atom, the random side chain being a linear, cyclic or branched alkyl group comprising 1 to 7 carbon atoms; and

wherein R1 – R3 are selected from the group consisting of hydrogen atoms and shorter or longer chains, the longer and shorter chains being selected from the group consisting of saturated or unsaturated, branched, cyclic or linear alkyl chains, aryl chains, alkaryl chains, arylalkyl chains, ester chains or ether chains; and wherein. the macromonomeric unit (b) is represented by formula (V):

$$P\text{–}(F_i)_s \quad (V)$$

wherein:

P represents a polymer chain having a number average molecular weight of 100 to 100000;

F_i represents a complementary reactive group in the macromonomeric unit (b) that is complementary reactive with another F_i of monomeric unit (a): and

s represents the number of these groups in the macromonomer and is 0 - 6 preferably 2 - 6.

12. Process according to claim 11, wherein the process proceeds by chain extension and wherein the following sets of monomeric unit (a) and macromonomeric unit (b) are polymerised:

(a) F_1-4H-F_1 and F_3-P-F_3;

(b) F_1-4H-F_2 and F_3-P-F_3;

(c) F_1-4H*-F_1 and F_3-P-F_3; or

(d) F_1-4H*-F_2 and F_3-P-F_3

wherein the couples F_1 - F_3 and F_2 - F_3 are complementary reactive groups.

13. Process according to claim 12, wherein the reactive groups F_i are selected from the group consisting of $-NH_2$, -NHR, -NCO, blocked -NCO, -OH, -C(O)OH, -C(O)OR wherein R is a linear or branched C_1-C_6 alkyl group, a C_6 - C_{12} arylgroup, a C_7 - C_{12} alkaryl group or a C_7 - C_{12} alkylaryl group, or R is halogen atom selected from the group consisting of Cl, Br or I.

14. Process according to any one of claims 11 - 13, wherein two or more macromonomeric units (b) having a different number average molecular weight are used.

15. Process according to any one of claims 11 - 14, wherein two or more macromonomeric units (b) having a different molecular structure are used.

16. Process according to any one of claims 11 - 15, wherein the monomeric unit (a) and/or the macromonomeric unit (b) comprises a "stopper" moiety having the formula P-F_1, 4H-F_1 of 4H*-F_1, wherein F_1, 4H and 4H* are as defined in the preceding claims.

17. Process according to any one of claims 11 – 16, wherein branching species of monomeric unit (a) or macromonomeric unit (b) are used, said branching species having the formula P-$(F_i)_u$ or 4H-$(F_i)_u$ or 4H*-$(F_i)_u$, wherein u is 3 - 6.

18. Process according to any one of claims 11 - 17, wherein the molar ratio between monomeric unit (a) and macromonomeric unit (b) is between 1:2 and 2:1.

19. Process according to claim 11, wherein the process proceeds by redistribution and wherein the following sets of monomeric unit (a) and macromonomeric unit (b) are polymerised:

(a) F_1-4H-F_1 and P; or

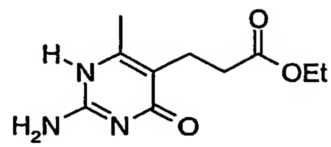
(b) F_1-4H-F_2 and P

wherein F_1, F_2 and P are as defined in the preceding claims.

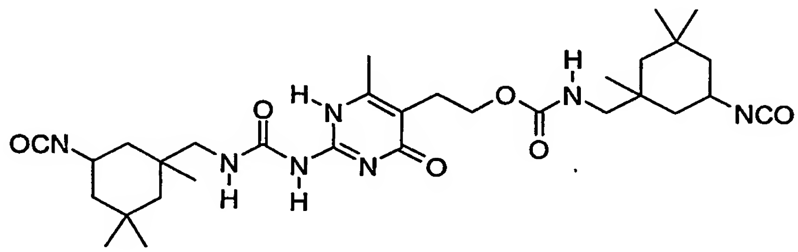
20. Process according to claim 19, wherein P has an number average molecular weight of 5000 - 100000.

21. Process according to claim 19 or claim 20, wherein the molar ratio between monomeric unit (a) and macromonomeric unit (b) is between 3:1 and 10:1.

22. Process according to any one of claims 11 – 21, wherein the monomeric unit (a) is



23. Process according to any one of claims 11 – 21, wherein the monomeric unit (a) is



24. A supramolecular polymer comprising quadruple hydrogen bonding units within the polymer backbone, wherein at least a monomer comprising a 4H-unit is incorporated in the polymer backbone via at least two reactive groups, provided that the 4H-units are not covalently incorporated in the polymer backbone through one or more silicon-carbon bonds, said supramolecular polymer being obtainable by the process according to any one of claims 11 - 23.

25. Use of a supramolecular polymer according to claims 1 - 10 or 24 in personal care applications, surface coatings, imaging technologies, biomedical applications, (thermo)reversible coatings, adhesive and sealing compositions and as thickening agents, gelling agents and binders.

Statement under Art. 19(1) PCT

Guan et al., Polymeric Preprints **2003**, *44(2)*, 485 – 486, discloses a supramolecular polymer wherein 4H-units are incorporated in a polymer backbone via positions 2 and 6 of the pyrimidone ring, wherein the polymer is prepared by reacting 1,4-diisocyanatohexane with 1-[6-(hydroxybutyl)-4-oxo-1,4-dihydro-pyrimidin-2-yl]-3-(3-hydroxypropyl)urea, the latter being a monomer having two identical reactive OH groups.